UNIVERSITY OF PENNSYLVANIA

THE STRUCTURE OF THIN FILMS OF METALLIC OXIDES AND HYDRATES

NEWBERN SMITH

A DISSERTATION

IN PHYSICS

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

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[Contribution from the Randal Morgan Laboratory of Physics, University of Pennsylvania]

The Structure of Thin Films of Metallic Oxides and Hydrates

By Newbern Smith

Iron is known to form a number of different oxides and hydrates, which differ chemically as well as physically. Oxide films have been removed from the surfaces of heated and passive iron by U. R. Evans,[1] using both chemical and electrolytic corrosion. He stated that the films consist for the most part of non-magnetic ferric oxide, but left unsettled the question of their contamination with hydroxides or other oxides of iron. It is possible that such contamination, as well as any pseudomorphism or peculiarities of structure of the films, of the kind suggested by Tammann,[2] may well affect the corrosion of the metal.

Save for Thomson's original article,[3] a few experiments of Boas and Rupp on passive iron,[4] and an investigation of the corrosion of iron by J. Cates,[5] no electron diffraction studies of iron oxide or hydroxide films have been reported in the literature.

The primary object of this research was to investigate by electron diffraction the nature and structure of the oxide film which forms on iron on warming in air, and to correlate the results with data obtained from studies of films formed on other metals and on the surfaces of solutions of metallic salts.

(1) Evans, *J. Chem. Soc.*, 1020 (1927); 2651 (1929).
(2) Tammann, *Stahl und Eisen*, **42**, 617 (1922).
(3) Thomson, *Proc. Roy. Soc.* (London) **128**, 649 (1930).
(4) Boas and Rupp, *Ann. Physik*, **13**, 1 (1932).
(5) Cates, *Trans. Faraday Soc.*, **29**, 817 (1933).

Experimental

Apparatus.—The electron diffraction camera used has been described in another article.[6] Thirty to fifty kilovolts were used in obtaining the diffraction patterns. A gold foil pattern was photographed, as a standard of comparison, for every pattern obtained from an unknown substance. Each film to be investigated was mounted on a specimen holder consisting of a thin brass disk pierced by 0.1-mm. holes. This hole served as the final collimating hole for the electron beam.

Preparation of Specimens.—A thin strip of the metal whose oxide film was to be removed was made the anode in an electrolytic cell consisting of three petrie dishes connected by strips of absorbent cotton. The electrodes and electrolyte were placed in the end dishes, while the middle dish was filled with a solution of the metallic chloride or sulfate, in order to hinder the migration of the cathodically produced hydroxyl ions. A current density of about 10 m. a. per sq. cm. was sufficient to undermine the film, which was then loosened by a much larger current. The isolated film was prepared for mounting by washing in several changes of water.

(6) Morgan and Smith, *Rev. Sci. Inst.*, **6**, 316 (1935).

Solutions of certain metallic salts acquire, on standing in air, thin surface films, due to the action of gases in the atmosphere. Such films were grown by exposing the solutions to the action of gases like ammonia or hydrogen sulfide. Thin films of the same type were also obtained by permitting cathodically produced alkali to diffuse through solutions of metallic salts. Extreme difficulty was experienced in washing and drying these "artificial" films, because of their great fragility.

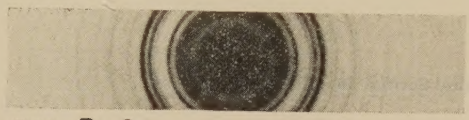

FIG. 1 Fe_3O_4

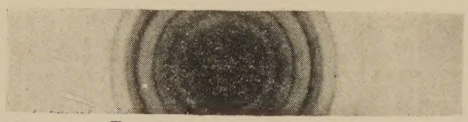

FIG. 4 γ-Fe OOH

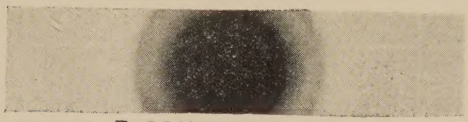

FIG. 5 γ-Fe OOH HEATED TO 355°C.

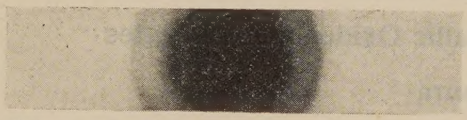

FIG. 6 γ-FeOOH HEATED TO 400°C.

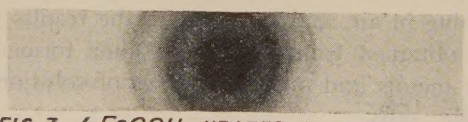

FIG. 7 γ-FeOOH HEATED TO 440°C.

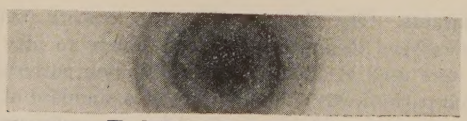

FIG. 8 γ-FeOOH HEATED TO 560°C.

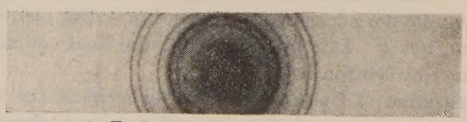

FIG. 9 γ-FeOOH HEATED TO 620°C.

Mounting and Treatment of Specimens.—After washing, the specimens were ordinarily floated in a mixture of water and ethyl alcohol. The use of carbon tetrachloride was found to be advantageous in mounting the more fragile films. The specimen holder was dipped into the solution and removed with the film caught squarely across the 0.1-mm. hole.

Some of the specimens were heated in an electric oven in order to determine the transformations they would undergo. Heat treatment could be carried only to about 620°, since the specimen holders corroded at higher temperatures.

Analysis of the Patterns.—Since the majority of thin films are polycrystalline in nature, with more or less random orientation of crystals, only the Hull–Debye–Scherrer ring diffraction patterns were usually obtained.

The plane spacings of the crystals composing the films were calculated in the usual way from the Bragg relation. In lieu of measuring the distance from the specimen to the photographic plate, and in order to eliminate any systematic errors in voltage measurement, the apparatus was calibrated each time in terms of the pattern given by a standard gold foil specimen. The lattice constant of the gold was taken as 4.070 Å.[7]

The diffraction patterns were represented schematically on logarithmic diagrams in the usual manner, with the heights of the lines roughly proportional to the estimated intensities of the rings. These diagrams were compared with those for the x-ray patterns, or were fitted to the appropriate Hull–Davey chart.

The sizes of the crystals composing the films were in some cases approximated by the use of the Debye–Scherrer formula connecting particle size with breadth of diffraction rings.[8] This formula is applicable only where the crystals belong to the cubic system, and are of uniform size, with undistorted lattices. These conditions are believed to have been satisfied, for the most part, in the thin films. In any case, the formula can give a lower limit to the sizes of the crystals.

Results

Films Removed from Iron.—Polished strips of electro-deposited iron were heated in air until first order interference colors appeared. The oxide films were then removed by electrolytic corrosion in an electrolyte of saturated potassium sulfate solution. Most of the films were transparent, but some were covered with particles of rust.

Figure 1 shows the diffraction pattern given by one of the films. Figure 2 gives the schematic diagrams for this pattern and for the x-ray pattern of ferrosic oxide (Fe_3O_4),[9] together with the spacings calculated from the known structure of ferrosic oxide.[7] Save for a few details, the diagrams are in good agreement. The lattice constant for the iron oxide film was calculated to be 8.37 ± 0.01 Å. (mean of seven plates), as compared with that of 8.372 Å. given by Wyckoff[7] for ferrosic oxide.

Although the agreement between the patterns is good, it is not proof that the iron oxide films con-

(7) Wyckoff, "The Structure of Crystals," Chemical Catalog Co., New York City, 1931.

(8) Randall, "The Diffraction of X-rays and Electrons by Amorphous Solids, Liquids, and Gases," John Wiley and Sons Inc., New York City, 1934; Ott, "Handbuch der Exp. Physik," Vol. VII (2. Teil), p. 297.

(9) Groebler, *Z. Physik*, **48**, 568 (1928); Bragg, *Phil. Mag.*, **30**, 305 (1915); Hedvall, *Z. anorg. allgem. Chem.*, **120**, 327 (1922).

sist of ferrosic oxide, since ferromagnetic ferric oxide (γ-Fe_2O_3) gives the same type of pattern as ferrosic oxide, and is generally believed to have the same lattice constant.[10] Some of the films were therefore heated in order to see whether any change occurred which might be attributed to the oxidation of ferrosic oxide in the film to γ-Fe_2O_3.

After heating to 600°, the films gave patterns which resembled more nearly those of γ-Fe_2O_3 films prepared by the dehydration of γ-ferric oxide monohydrate (γ-FeOOH), in that the innermost ring was relatively more intense than in the case of the original film, and the lattice constant was about 0.5% greater. It seems probable, therefore, that the oxide film removed from iron was for the most part ferrosic oxide, which changed, at least partially, to γ-Fe_2O_3 on heating.

These ferrosic oxide films were occasionally contaminated with other substances. The most frequent contamination was with γ-FeOOH, one of the end-products of rust. It seems likely that this arose from the rusting of small iron particles which had clung to the film. One film gave a very sharp pattern of the rhombohedral normal ferric oxide (α-Fe_2O_3). The α-Fe_2O_3 content of this film varied widely from point to point, and is not thought to have been produced by the original heat treatment.

All of the films removed from heated iron showed predominantly the structure of ferrosic oxide. The rings were always sharp, indicating that the crystals were at least 300 Å. in size. This is of the same order of magnitude as the thickness of the thinnest film, and indicates that the film may consist of a single layer of crystals. None of the films gave any evidence of preferred orientation of the crystals.

Strips of iron, polished but unheated, yielded no film, showing that no oxide film was formed during electrolytic treatment. All of the films removed from iron surfaces, therefore, are thought to have been formed before electrolytic treatment was begun.

(10) Welo and Baudisch, *Naturwissenschaften*, **13**, 752 (1925); *ibid.*, **14**, 1006 (1926); *Phys. Rev.*, **25**, 587 (1925); *Phil. Mag.*, **50**, 399 (1925); Thewlis, *ibid.*, **12**, 1087 (1931).

Films of γ-Ferric Oxide Monohydrate.—Dilute solutions of ferrous ammonium sulfate, exposed to the action of ammonia, acquired thin, transparent, greenish films, which turned brown on standing. The thickness of the films depended on the length of exposure to the ammonia.

In Fig. 4 is given the diffraction pattern obtained from one of these films, and in Fig. 3 the pattern is compared with the x-ray pattern of γ-FeOOH[11] and with the electron diffraction pattern of the mineral rubinglimmer (γ-goethite, or lepidocrocite).[5] The agreement between the patterns is fairly good. All of the rings which are designated by the Miller indices in Fig. 3 may be attributed to an orthorhombic structure with axes 3.82, 3.06 and about 12.5 Å. This resembles closely the structure given for γ-FeOOH.[12]

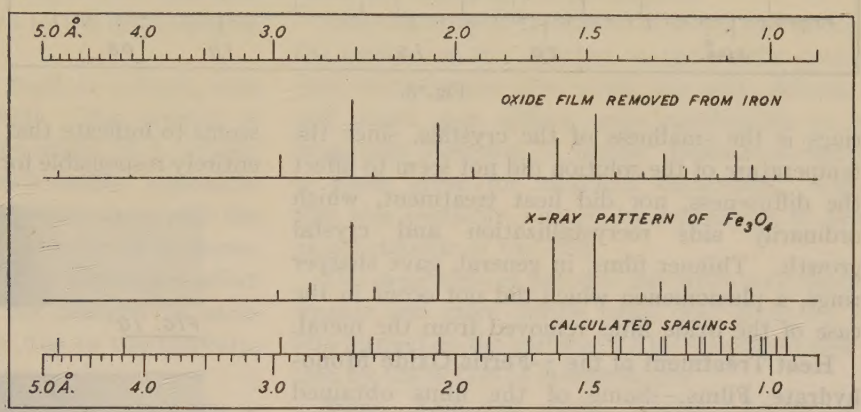

Fig. 2.

The lines marked "x" fail to occur in the x-ray diagram and correspond to the two most prominent rings of the ferrosic oxide structure. The presence of this oxide may be caused by the oxidation of portions of the surface of the ferrous ammonium sulfate solution prior to precipitation with ammonia, since ammonia is known to precipitate hydrous ferrosic oxide from solutions where ferric ions predominate.[13] The fact that these two rings vary in intensity and diffuseness in different specimens would lend support to this view.

The evidence thus indicates that the films are predominantly composed of γ-FeOOH. The composition of the films is thus similar to the composition of substances obtained by the precipitation and subsequent oxidation of ferrous hydroxide.[11,14]

(11) Böhm, *Z. anorg. allgem. Chem.*, **149**, 203 (1925); Williams and Thewlis, *Trans. Faraday Soc.*, **27**, 767 (1931).

(12) Böhm, *Z. Krist.*, **68**, 567 (1928).

(13) Hüttig and Möldner, *Z. anorg. allgem. Chem.*, **196**, 177 (1930).

(14) Schikorr, *ibid.*, **191**, 322 (1930).

The patterns given by these γ-FeOOH films were peculiar in that some of the rings were always more diffuse than others. This might be explained by considerations of lattice distortion or of the shape of the crystals. It is not thought that the primary reason for the diffuseness of the rings is the smallness of the crystals, since the temperature of the solution did not seem to affect the diffuseness, nor did heat treatment, which ordinarily aids recrystallization and crystal growth. Thinner films, in general, gave sharper rings, a phenomenon which did not occur in the case of the oxide films removed from the metal.

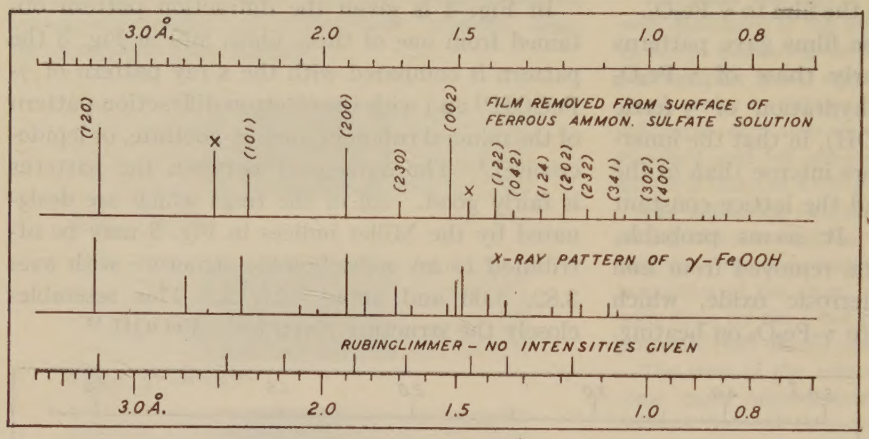

Fig. 3.

Heat Treatment of the γ-Ferric Oxide Monohydrate Films.—Some of the films obtained from the ferrous ammonium sulfate solutions were heated to a series of different temperatures in an electric oven in order to determine whether the heating produced the same transformations as are given in the literature for γ-FeOOH.[11,15] During this treatment, the films gradually changed in color from a light yellow to a dark reddish brown.

The progressive change in structure during the heat treatment is shown in Figs. 4 to 9. The γ-FeOOH pattern vanished above 200°, and was replaced by a very diffuse pattern with spacings and intensities similar to those given by the oxide film removed from iron. As the heat treatment proceeded, the rings became sharper, without any change in their relative spacings.

The differences that exist between this pattern and the patterns of the ferrosic oxide films removed from iron are similar to the changes that are produced by heating a film removed from iron. The innermost ring is relatively more intense than in the case of the ferrosic oxide film, and the lattice constant is about 0.8% greater, being 8.43 ± 0.02 Å. (mean of three plates). Because of these differences, and because heating in air is not a reducing process, and since the dehydration product of γ-FeOOH is known to be γ-Fe_2O_3,[11,16] it is concluded that the original film was γ-FeOOH, which passed into γ-Fe_2O_3 on heating.

The size of the crystals of γ-Fe_2O_3 obtained by dehydrating the γ-FeOOH film at 355° was roughly estimated to be of the order of 20 Å. This increased to over 300 Å. for films heated to 600°. The fact that growth occurred seems to indicate that smallness of the crystals is entirely responsible for the diffuseness of the rings.

FIG. 10

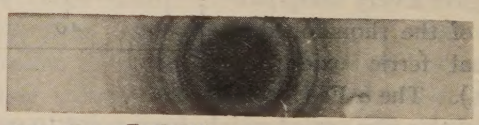

FIG. 11 α-FeOOH

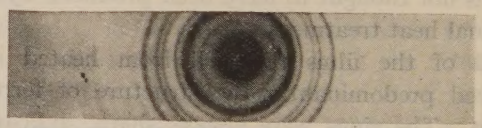

FIG. 12 α-Fe_2O_3

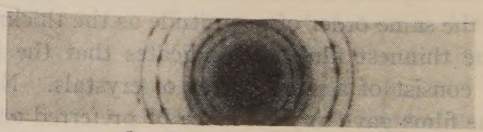

FIG. 13 Cu_2O

Due to the corrosion of the ordinary metal specimen holder, heat treatment could not be carried far enough to obtain the transformation of the cubic γ-Fe_2O_3 into the rhombohedral α-Fe_2O_3. The temperatures at which the changes in the films occurred cannot be regarded as trans-

(15) Sosman and Posnjak, *J. Wash. Acad.*, **15**, 329 (1925); Welo and Baudisch, *Phil. Mag.*, **17**, 753 (1934).

(16) Baudisch, *Science*, **77**, 317 (1933); Dudley, *Am. Chem. J.*, **28**, 61 (1902).

formation points, since the specimens were not held at any one temperature for sufficiently long periods.

Films Prepared from Ferric Ammonium Sulfate Solutions.—Dilute solutions of ferric ammonium sulfate, exposed to ammonia gas, acquired thin, brown films, which tended to dissolve as soon as the ammonia was removed. This tendency was the more marked, the greater the concentration of the solution.

The diffraction pattern obtained from one of these films is shown in Fig. 10. Five rings are measurable against the intense background. Four of these rings correspond to the four most prominent rings in the ferrosic oxide pattern. The fifth ring, because of its intensity and great diffuseness, was not believed to belong to this structure, and was tentatively assigned to the (200) spacing in the γ-FeOOH structure.

The film thus consists of Fe_3O_4 or γ-Fe_2O_3, with possibly a trace of γ-FeOOH. The crystals of the oxide are estimated to be about 50 Å. in size, and those of the hydrate much smaller, approaching amorphousness. These results agree with the work of Hüttig and Möldner[13] referred to above.

Heating these films to 200° in air did not affect the diffuseness of the rings, but changed the background somewhat, probably due to the dehydration of the hydrate.

Films of α-Ferric Oxide Monohydrate.—Immediately on completion of the electrolytic treatment of iron, a light brown skin usually formed on the surface of the solution in the anodic petrie dish. The diffraction pattern of this film is given in Fig. 11. Analysis of this pattern shows that the film has the same structure as the mineral goethite (α-FeOOH) as given by x-ray data.[11] This agrees with the results of G. Schikorr[14] on the oxidation and subsequent hydrolysis of a ferrous salt.

One of the α-FeOOH films, heated for a few moments in air at 400°, turned a dark reddish brown, and gave the diffraction pattern shown in Fig. 12. Analysis of this pattern shows that the film has a rhombohedral crystal structure identical with that given by the x-ray data for α-Fe_2O_3. This is further proof that the original film was α-FeOOH, since the α-hydrate is known to give the α-oxide on dehydration.

Films of Nickel Oxide and Hydroxide.—Strips of nickel, heated in air so as to show first order interference colors, were subjected to electrolytic corrosion in an electrolyte of saturated potassium chloride, and yielded transparent, greenish films, quite easy to handle and mount.

These films always gave excellent diffraction patterns, more than thirty measurable rings being recorded. All of the patterns indicated the structure of the oxide film to be that of normal nickelous oxide, with a lattice constant of 4.18 ± 0.01 Å., as compared to the x-ray value of 4.172 Å.[7] Darbyshire[17] and Preston[18] had determined the lattice constant by electron diffraction to be 4.10 Å.

One of the films, estimated to be less than 500 Å. in thickness because of the absence of interference colors, gave rings whose diffuseness indicated the crystals to be about 100 Å. in size. It is evident, therefore, that there can be at most but a few layers of crystals present.

After electrolytic treatment of nickel specimens, the surface of the solution in the anodic petrie dish yielded a thin film which was quite delicate, and which gave diffuse rings attributable to a hexagonal structure of lattice dimensions equal to those given for nickelous hydroxide.[7] This film was probably formed by hydrolysis of the nickel chloride in the dish.

The same type of pattern, but with very much weaker and more diffuse rings, was given by a film formed on the surface of a nickel sulfate solution by the action of ammonia gas.

Films Removed from Copper.—Strips of copper, heated in air to first order colors, yielded thick reddish films on electrolytic corrosion in saturated potassium sulfate solution.

The patterns given by these films were all of the type shown in Fig. 13, and correspond to the normal cuprous oxide structure, with a lattice constant of 4.28 Å. This agrees with Wyckoff's value,[7] but is somewhat higher than that given by Neuburger.[19] The differences may be due to impurities.

The intense spots on the rings do not indicate any orientation of the crystals, but do indicate the presence of a number of fairly large crystals along with the usual microcrystalline structure. Apparently large crystals are forming at the expense of the smaller ones, even in the thin films dealt with here. The occurrence of spots in pairs indicates imperfections in the crystals whereby reflection can occur from both sides of a set of crystal planes.

(17) Darbyshire, *Trans. Faraday Soc.*, **27**, 675 (1931).
(18) Preston, *Phil. Mag.*, **17**, 466 (1934).
(19) Neuburger, *Z. Physik*, **67**, 845 (1931).

Strips of copper, polished but unheated, acquired reddish-brown surface films on electrolytic treatment in saturated potassium sulfate solution. These films were loosened in the same manner as were those produced by heat. The copper surface underneath was pitted, and differed from the polished surface in that further electrolytic treatment did not cause such a film to form again. Only low current densities could be used, as higher ones destroyed the film.

These films gave the patterns of cuprous oxide, with metallic copper superimposed. The cuprous oxide had a normal lattice constant, but that of the copper was expanded by 1.5%. It is possible that this effect might be caused by the entrance of oxygen atoms into the copper lattice.

Conclusions

All of the oxide films removed from heat tinted metal surfaces were crystalline, and had crystals large enough to give sharp diffraction rings. The evidence indicates that the thinner of these films may consist of single layers of crystals. No preferred orientation of crystals was observed in any case.

x-Ray examination of thicker films on iron and copper[20] has shown the presence of an orientation and pseudomorphism in the films depending on the nature of the underlying crystalline surface. The lack of orientation observed in the present experiments is probably due to the amorphous nature of the highly polished surface. Oxidation to a depth of 10^{-5} cm. or so would probably not be sufficient to penetrate this layer.

The oxide films removed electrolytically from iron heated in air had the crystal structure common to the two magnetic oxides, Fe_3O_4 and γ-Fe_2O_3. The evidence indicates that the oxide was mostly Fe_3O_4. The complexity of the oxides formed by iron, and the difficulty of preparing pure samples of the higher oxides and hydroxides for comparison, makes the positive identification of the films quite difficult. In view of the ease with which contamination occurred, it is believed that most of the films were mixtures of several substances, with only one or two present in sufficient quantity to give diffraction rings. It is entirely possible, for example, for oxygen atoms to be distributed throughout a film of Fe_3O_4 in such a way as to make it, at certain points, a film of γ-Fe_2O_3.

(20) Mehl, McCandless and Rhines, *Nature*, **134**, 1009 (1934).

Evans[1] stated that the main portion of the oxide film was of non-magnetic ferric oxide. He later observed[21] that certain films exhibited weak magnetic properties, but believed them to be of γ-Fe_2O_3, rather than of Fe_3O_4. The results of this work, however, show that the films are always composed of magnetic oxide. The relative stability of Fe_3O_4 may explain some of the properties of the iron oxide films as inhibitors of corrosion.

Earlier investigation of the structure of thick oxide skins on iron,[22] such as are formed during the production of the Bower–Barff protective coating, showed the presence of layers of each of the three oxides FeO, Fe_3O_4 and Fe_2O_3, with the inner FeO as the thickest part of the skin. Pfeil[23] and others also found the thick heat scale on iron to consist of varying mixtures of FeO and Fe_2O_3, and are inclined to regard the scale as consisting of a series of solid solutions of the oxides. In the present experiments oxidation took place for only a few seconds and could not affect more than the surface of the iron, producing a film of the order of 1/1000 as thick as these scales. It is quite possible that the FeO phase, if present, is extremely thin (of the order of a few atoms) and would not manifest itself in an ordinary diffraction photograph.

Although Fe_3O_4 and γ-Fe_2O_3 are usually regarded as indistinguishable by crystallographic means, γ-Fe_2O_3 films prepared by two different methods were found to give more intense (111) rings and to have somewhat larger lattice constants than in the case of Fe_3O_4. This may indicate a real structural difference, or it may indicate that the method of preparation of the substances affects their structures.

The oxide films removed from the surfaces of nickel and copper after heating them in air have the normal structure of nickelous and cuprous oxides, respectively, and the lattice constants agree quite well with those determined by x-ray measurements.

Growth of large crystals at the expense of smaller ones is apparently a characteristic of cuprous oxide, since relatively large crystals, which are known to be present in thick layers of the oxide, were also found to be present in thin films.

The fact that electrolytic treatment forms a film of cuprous oxide on polished copper would seem to throw a little doubt on the conclusion that all films produced on copper by heating, and

(21) Evans, *J. Chem. Soc.*, 478 (1930).
(22) Bozorth, THIS JOURNAL, **49**, 967 (1927).
(23) Pfeil, *Heat Treating and Forging*, **15**, 734 (1929).

later removed electrolytically, are necessarily of this oxide. Any other oxide which was present may well have been changed to cuprous oxide by the electrolytic process.

In this relation the question may also be raised as to whether the electrolytic treatment might not change the oxide films on other metals. To be sure, a change in the structure of the copper oxide film during electrolysis would not necessarily imply that there would be a change in a film of iron or nickel oxide. For one thing, the metals occupy different positions in the electrochemical series. Nevertheless, the question of the identity of the films before and after electrolytic treatment would seem to offer an interesting problem for further research.

Films of metallic hydroxides and hydrates formed on the surfaces of liquids have essentially the same structure and chemical properties as do the hydrates precipitated from the same liquids by the same reagents. The diffraction rings given by the films were usually rather diffuse, indicating that the crystals were smaller than the crystals in the films removed from metals. This is to be expected, in view of the gelatinous nature of precipitated hydroxides. The fact that some rings are more diffuse than others might be attributed to the shape of the crystals, due to the manner of their growth. Because of the peculiarities of shape, and the possibility of lattice distortion, no good estimate can be made of the size of the crystals. It would seem, however, that the crystals are considerably smaller than the thickness of the films, for most of the films showed first and second order colors, while the rings were still diffuse, and not at all spotty.

The writer wishes to thank Dr. William Blum, of the National Bureau of Standards, Washington, D. C., for the gift of the electro-deposited iron used in these experiments. The writer also gratefully acknowledges his indebtedness to Dr. Raymond Morgan, of the Physics Department, University of Pennsylvania, for suggesting this research, and for many helpful suggestions throughout the work.

Summary

1. The structures of thin films of metallic oxides, hydroxides and hydrates, prepared in various manners, were investigated by the method of electron diffraction.

2. Oxide films removed from heated metals were found to be polycrystalline, consisting of relatively large crystals of the normal metallic oxides: nickelous oxide, in the case of nickel, cuprous oxide, in the case of copper, and predominantly ferrosic oxide in the case of iron. Estimates of crystal sizes in the films indicate that they consist of only a few layers—possibly even but a single layer—of crystals. The films showed no indications of preferred orientation or of pseudomorphism. In one case evidence of lattice distortion during the oxidation process was found.

3. Films of hydroxides and hydrates precipitated from solutions of metallic salts were found to be always crystalline, but usually with quite small crystals, approaching amorphousness. The crystals also showed evidence of lattice distortion, arising probably from the manner of their formation.

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